Appendix J Air Monitoring and Sampling Methods

This appendix contains a summary of monitoring and sampling methods for a variety of organic and inorganic compounds in ambient air. Each approach is described briefly, with a listing of compounds for which it is appropriate, the detection limit, and a summary of advantages and disadvantages in using the approach. Descriptions of the methods can be downloaded from the EPA's Ambient Monitoring Technology Information Center (AMTIC) website (www.epa.gov/ttn/amtic/airtox.html).

The measurement process generally relies on collecting a sample in the field, followed by a return to the lab for analysis. A number of methods are used for initial collection of samples in the field:

1. **Sampling tubes**, in which air is drawn through a tube containing a sorbent specific to the compound being sampled, and the tube returned to the lab for analysis. Possible sorbents in the tube are organic polymers; carbon (molecular, activated, etc); polyurethane foam; silica gel; and dinitrophenylhydrazone (DNPH). Multi-sorbents also are available.

2. **Filters**, in which air is drawn through a fiber (often a glass fiber) filter, collecting the sampled compound, and returned to the lab for analysis. In some methods, air is drawn over an absorbent onto which the chemical sorbs. In some methods, a chemical reaction occurs that converts the air toxics to another material that is then analyzed.

3. **Cryogenic traps**, in which air is drawn into a chamber at low temperature, condensing the compound out of the air. The trap and condensate are returned to the lab for analysis.

4. **Evacuated chambers**, in which air is drawn into a chamber under vacuum. The chamber is returned to the lab for analysis.

An important consideration in the use of such methods is the available time between collection and analysis of samples. The compounds will degrade during the intervening holding period, and so this holding period should not exceed maximum allowed times (holding times depend on the method and compound (consult the AMTIC website for information on QA/QC for air monitoring).

Method Designation	Applicable Compounds	Approach	Detection Limit	Advantages	Disadvantages
TO-1	VOCs (80º to 200º C); e.g. benzene, toluene, xylenes.	Ambient air is drawn through organic polymer sorbent where certain compounds are trapped. The cartridge is transferred to the lab, thermally desorbed and analyzed using GC/MS or GC/FID.	0.01 to 100 ppbv	Good data base; large sample volume; water vapor not collected; wide variety of compounds collected; low detection limits; standard procedures available; practical for field use.	Highly volatile compounds and certain polar compounds not collected; rigorous clean-up of absorbent required; no possibility of multiple analyses; low breakthrough volume for some compounds; desorption of some compounds difficult; interference from structural isomers; possible contamination of sorbent and blank; artifact formation.
TO-2	Highly volatile VOCs (-15º to 120º C); e.g. vinyl chloride, chloroform, chlorobenzene.	Selected volatile organic compounds are captured on carbon molecular sieve absorbents. Compounds are thermally desorbed and analyzed by GC/MS or GC/FID techniques.	0.1 to 200 ppbv	Trace levels of VOCs are collected and concentrated; efficient collection of polar compounds; wide range of application; highly volatile compounds are absorbed; easy to use in field.	Some trace levels of organic species are difficult to recover from sorbent; interferences from structural isomers; water is collected and can de-activate absorption sites; thermal desorption of some compounds difficult.
TO-3	Nonpolar VOCs (-10º to 200º C); e.g. vinyl chloride, methylene chloride, acrylonitrile.	Vapor phase organics are condensed in a cryogenic trap. Carrier gas transfers the condensed sample to a GC column. Absorbed compounds are eluted from the GC column and measured by FID or ECD.	0.1 to 200 ppbv	Collects a wide variety of VOCs; standard procedures are available; contaminants common to absorbent materials are avoided; low blanks; consistent recovery; large data base.	Moisture levels in air can cause freezing problems in cryogenic trap; difficult to use in field; expensive; integrated sampling is difficult; compounds with similar retention times interfere.
TO-4	Pesticides and PCBs; e.g. PCBs, 4,4-DDE, DDT, DDD.	Pesticides/PCBs trap on filter and PUF absorbent trap. Trap is returned to lab, solvent extracted and analyzed by GC/FID/ECD or GC/MS.	0.2 pg/m^3 to 200 ng/m^3	Low detection limits; effective for broad range of pesticides and PCBs; PUF reusable; low blanks; excellent collection and retention efficiencies for common pesticides and PCBs.	Breakdown of PUF absorbent may occur with polar extraction solvents; contamination of glassware may increase detection limits; loss of some semi-volatile organics during storage; interference by extraneous organics; difficulty in identifying individual pesticides and PCBs if ECD used.
TO-5	Aldehydes and Ketones; e.g. formaldehyde, acetaldehyde, acrolein.	Air sample is drawn through DNPH impinger solution using a low volume pump. The solution is analyzed using HPLC with a UV detector.	1 to 50 ppbv	Specific for aldehydes and ketones; good stability for derivative compounds formed in the impingers; low detection limits.	Sensitivity limited by reagent purity; potential for evaporation of liquid over long term sampling; isomeric aldehydes and ketones may be unresolved by the HPLC system.

Method Designation	Applicable Compounds	Approach	Detection Limit	Advantages	Disadvantages
TO-6	Phosgene	Ambient air is drawn through a midget impinger containing 10 ml of 2/98 aniline/toluene (v/v). Phosgene reacts with aniline to form 1,3-diphenylurea and is analyzed using reverse-phase HPLC with a UV absorbance detector operating at 254 nm.	1 to 50 ppbv	Good specificity; good stability for derivative compounds formed in the impingers; low detection limits.	Chloroformates and acidic materials may interfere; contamination of aniline reagents may interfere; use of midget impingers in field application may not be practical.
TO-7	N-nitroso dimethylamine	Ambient air is drawn through a cartridge containing Thermosorb/N absorbant to trap N-nitrosodimethyl amine. The cartridge is returned to the lab and eluted with 5 ml of dichloromethane. The cartridge then is eluted in reverse direction with 2 ml of acetone. The N-nitrosodimethylamine is determined by GC/MS.	1 to 50 ppbv	Good specificity; good stability for derivative compounds formed on the cartridge; low detection limit for n-nitrosodimethylamine; placement of sorbent as first compound in sample train minimizes contamination; sampling system portable and lightweight.	Compounds with similar GC retention times and detectable MS ions may interfere; specificity is a limiting factor if looking for other organic amines.
TO-8	Cresol and phenol	Ambient air is drawn through two midget impingers. Phenols are trapped as phenolates in NaOH solution, which is returned to the lab and analyzed by HPLC.	1 to 250 ppbv	4,6-dinitro-2-methylphenol specific to class of compounds; good stability; detects non-volatile as well as volatile phenol compounds.	Compounds having the same HPLC retention times may interfere; phenolic compounds of interest may be oxidized; limited sensitivity.
TO-9A*	Dioxin, furan and PCBs	Ambient air is drawn through a glass fiber filter and a polyurethane foam (PUF) absorbent cartridge with a high volume sampler. The filter and PUF cartridge are returned to the lab and extracted using toluene. The extract is concentrated using the Kudrena-Danish technique, diluted with hexane, and cleaned up using column chromatography. The cleaned extract then is analyzed by high resolution GC/high resolution MS.	0.25 to 5000 pg/m^3	Cartridge is reusable; excellent detection limits; easy to preclean and extract; excellent collection and retention efficiencies; brad database; proven methodology.	Analytical interferences may occur from PCBs, methoxybiphenyls, chlorinated hydroxydiphenylethers, napthalenes, DDE and DDT with similar retention times and mass fractions; inaccurate measurement Ds/Fs are retained on particulate matter and may chemically change during sampling and storage; analytical equipment required (HRGC/HRMS) expensive and not readily available; operator skill level important; complex preparation and analysis process; can't separate particles from gas phase.

Method Designation	Applicable Compounds	Approach	Detection Limit	Advantages	Disadvantages
TO-10A	Pesticides; e.g. heptachlor, chlordane, dieldrin, aldrin	A low volume sample (1-5 L/min) is pulled through a PUF plug to trap organochlorine pesticides. After sampling, the plug is returned to the lab, extracted and analyzed by GC coupled to multi-detectors (ECID, PID, FID, etc).	1 to 100 ng/m^3	Easy field use; proven methodology; easy to clean; effective for broad range of compounds; portable; good retention of compounds.	ECD and other detectors (except MS) are subject to responses from a variety of compounds other than target analytes; PCBs, dioxins and furans may interfere; certain organochlorine pesticides (e.g. chlordane) are complex mixtures and can make accurate quantification difficult; may not be sensitive enough for all target analytes.
TO-11A	Formaldehyde, other aldehydes and ketones; e.g. formaldehyde, acetaldehyde, acrolein.	An ambient air sample is drawn through a DNPH cartridge at a rate of 500 to 1200 ml/minute. The cartridge is returned to the lab in screw-cap glass vials. The cartridge then is removed from the vial and washed with acetonitrile by gravity feed elution. The eluate is diluted volumetrically and an aliquot is removed for determination of the DNPH-formaldehyde derivative by isocratic reverse phase HPLC with UV detection at 350 nm.	0.5 to 100 ppbv	Placement of sorbent as first element in the sampling train minimizes contamination; large database; proven technology; sampling system is portable and lightweight.	Isometric aldehydes and ketones and other compounds with the same HPLC retention time as formaldehyde might interfere; Carbonyls on the DNPH cartridge may degrade if an ozone denuder is not used; liquid water captured on the DNPH cartridge during sampling may interfere; ozone and UV light deteriorates trapped carbonyls on cartridge.
TO-12	Non-methane organic compounds (NMOC)	Ambient air is drawn into a cryogenic trap, where the non-methane organic compounds (NMOCs) are concentrated. The trap is heated to move the NMOCs to the FID. Concentration of NMOCs is determined by integrating under the broad peak. Water correction is necessary.	0.1 to 200 ppmvC	Standard procedures are available; contaminants common to absorbent materials are avoided; low blanks; consistent recoveries; large data base; good sensitivity; useful for screening areas or samples; analysis much faster than GC.	Moisture levels in air can cause freezing problems; non-speciated measurement; precision is limited.
TO-15	VOCs (polar and non-polar); methanol, benzene, xylene, nitrobenzene	Whole air samples are collected in a specifically-prepared canister. VOCs are concentrated on a solid sorbent trap or other arrangement, separated on a GC column, and passed to an MS detector for identifaction and quantification.	0.2 to 25 ppbv	Incorporates a multi-sorbent/dry purge technique to manage water; has established methods performance criteria; provides enhanced provisions for QC; unique water management approach allows analysis of polar VOCs.	Expensive analytical equipment; depends critically on operator skill level.

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TO-16	Polar and non-polar VOCs; e.g. alcohols, ketones, benzene, toluene, o-xylene, chlorobenzene.	VOCs are monitored using real-time long-path open-path Fourier transform infrared spectroscopy (FTIR).	25 to 500 ppbv	Open path analysis maintains integrity of samples; multi-gas analysis saves money and time; path-integrated pollutant concentration measurement minimizes possible sample contamination and provides real-time pollutant concentration; applicable for special survey monitoring; monitoring at inaccessible areas possible using open-path FTIR.	High levels of operator skill required; requires spectra interpretation; Limited spectral library available; higher detection limits than most alternatives; must be skilled in computer operation; substantial limitations from ambient CO_2 and humidity levels associated with spectral analysis.
TO-17	Polar and non-polar VOCs; e.g. alcohols, ketones, benzene, toluene, o-xylene, chlorobenzene.	Ambient air is drawn through a multi-bed sorbent tube where VOCs are trapped. The cartridge is returned to the lab, thermally desorbed and analyzed by GC/MS or other methods.	0.2 to 25 ppbv	Placement of the sorbent as the first element minimizes contamination from other sample train components; large selection of sorbents to match with target analyte list; includes polar VOCs; better water management using hydrophobic sorbents than Compendium Method TO-14A; large database; proven technology; size and cost advantages in sampling equipment.	Distributed volume pairs required for quality assurance; rigorous clean-up of sorbent required; no possibility of multiple analysis; must purchase thermal desorption unit for analysis; desorption of some VOCs is difficult; contamination of absorbent can be a problem.
IO-1	Suspended particulate matter (SPM); continuous measurement.	Ambient air is drawn at a rate of approximately 16 to 17 L/minute through a virtual impact or cyclonic flow filter. Particle build-up on a filter tape is determined continuously either through measurement of attenuation of beta particles incident on the tape or through an oscillating pendulum.	3 micrograms/m^3.	Less sensitive to temperature, pressure and humidity fluctuations than other continuous methods.	Results can be biased by water collection on the filter tape; oscillator must be isolated from external noise and vibrations.
IO-2	Suspended particulate matter (SPM); integrated measurement.	Ambient air is drawn through a filter with a high volume sampler, with large (> 10 micron) particles removed prior to the filter. The filter is weighed before and after sampling, with dessication to remove water vapor. Mean particulate concentration is determined from mass gain and air flow rate.	1 microgram/m^3	Well established methodology; relatively simply technique to employ	Balance used in measurement must be precise; subject to bias due to collection of water vapor if complete dessication is not obtained;

Method Designation	Applicable Compounds	Approach	Detection Limit	Advantages	Disadvantages
IO-3	Chemical species analysis of filter-collected SPM.	Ambient air is drawn through a filter with a high volume sampler, with large (> 10 micron) particles removed prior to the filter. The filter is weighed before and after sampling, with dessication to remove water vapor. The filter then is subsampled and strips digested using a microwave or hot acid extraction technique. Specific extracts are analyzed by the appropriate method.	Depends on compound considered.	Advantages depend on chemical species analyzed, but particle collection has the advantages noted in IO-2.	Disadvantages depend on chemical species analyzed.
IO-4	Reactive acidic and basic gases; strong acidity of atmospheric fine particles. HNO_3, NH_3, HCL, SO_2, NH_4, SO_4, NO_3	Based on measurement of the fine particle strong acidity component of the atmosphere. Air is drawn through an annular denuder followed by a 37 mm Teflon filter to trap the fine particle acid aerosol. The filter is returned to the lab for extraction and analysis using an aequeous solution of perchloric acid followed by titration or pH determination.		Simple method of analysis; well established methodology.	Without denuders employed to remove ammounia and other acid gases, interference can occur.
IO-5	Atmospheric mercury	Low flow (for vapor phase) or higher flow (for particulate phase) ambient air stream is flowed over gold coated bead traps and glass fiber filters. Mercury content is determined by cold-vapor atomic fluorescence spectrometry after thermal desorption.	30 pg/m^3 (particulate phase) or 45 pg/m^3 for vapor phase.	No known positive interferences using the 253.7 nm wavelength to excite the mercury atoms.	Possible interferences from PAHs and water vapor; excessive water quenches signal; free halogens can degrade trap.